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14. ABSTRACT

Regular two-dimensional covalent grids of monolayer thickness with molecular-size openings, reminiscent of a tennis net or chickenwire, will have many useful applications, among others as selective barrier materials and efficient passive or active separation membranes. We propose to synthesize a grid whose basic unit is Zn(II) porphyrin triply linked in the meso-meso, and both ?-? positions four times by carbon-carbon bonds to each of its neighbors to form porphite sheets a grid-type material that would be an analog of graphene.. The resulting grid would be conducting, have an electronic band structure and well-defined pores. We report the development of protocols for the meso-meso linking of Zn(II) porphyrin at the air-water

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Molecular Grid Membranes

ABSTRACT

Regular two-dimensional covalent grids of monolayer thickness with molecular-size openings, reminiscent of a tennis net or chickenwire, will have many useful applications, among others as selective barrier materials and efficient passive or active separation membranes. We propose to synthesize a grid whose basic unit is Zn(II) porphyrin triply linked in the meso-meso, and both ?-? positions four times by carbon-carbon bonds to each of its neighbors to form porphite sheets a grid-type material that would be an analog of graphene.. The resulting grid would be conducting, have an electronic band structure and well-defined pores. We report the development of protocols for the meso-meso linking of Zn(II) porphyrin at the air-water interface using Langmuir-Blodgett methods with a resulting polymer net whose MW weight exceeds 10,000 daltons and methods for assaying the extent of the interfacial polymerization. Towards the goal of full synthesis of porphite, we report the meso-meso linking of Zn(II) porphyrin at the air-water interface using Langmuir-Blodgett methods with a resulting polymer net whose MW exceeds 10,000 daltons.

List of papers submitted or published that acknowledge ARO support during this reporting period. List the papers, including journal references, in the following categories:

(a) Papers published in peer-reviewed journals (N/A for none)

Pospíšil, L.; Varaksa, N.; Magnera, T. F.; Brotin, T.; Michl, J. "Adsorption of Tentacled Tetragonal Star Connectors, C4R4-Co-C5(HgX)5, on Mercury", Langmuir 2007, 23, 930.

Horansky, R. D.; Magnera, T. F.; Price, J. C.; Michl, J. "Artificial Dipolar Molecular Rotors", in Controlled Nanoscale Motion, Lecture Notes in Physics, Vol. 711, Linke, H.; Månsson, A., Eds., Springer: Berlin and Heidelberg, 2007, p 303.

Vacek, J.; Michl, J. "Artificial Surface-Mounted Molecular Rotors: Molecular Dynamics Simulations", Adv. Funct. Mater. 2007, 17, 730.

Number of Papers published in peer-reviewed journals: 3.00

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(c) Presentations

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Gordon Conference on Electrochemistry, Santa Ynez Valley Marriott, Buellton, CA, Feb. 12-17, 2006

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Graduate Students

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Deborah Casher	0.25
FTE Equivalent:	**0.25**
Total Number:	**1**

Names of Post Doctorates

NAME	PERCENT_SUPPORTED
Thomas Magnera	1.00
FTE Equivalent:	**1.00**
Total Number:	**1**

Names of Faculty Supported

NAME	PERCENT_SUPPORTED
FTE Equivalent:	
Total Number:	

Names of Under Graduate students supported

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FTE Equivalent:	
Total Number:	

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The number of undergraduates funded by your agreement who graduated during this period and will continue to pursue a graduate or Ph.D. degree in science, mathematics, engineering, or technology fields:...... 0.00

Number of graduating undergraduates who achieved a 3.5 GPA to 4.0 (4.0 max scale):...... 0.00

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NAME

Total Number:

Names of personnel receiving PHDs

NAME

Total Number:

Names of other research staff

NAME   PERCENT_SUPPORTED

FTE Equivalent:
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Sub Contractors (DD882)

Inventions (DD882)

Statement of Problem Studied

Regular two-dimensional covalent grids of monolayer thickness with molecular-size openings, reminiscent of a tennis net or chickenwire, will be a novel type of material. One can anticipate many useful applications, among others as selective barrier materials and efficient passive or active separation membranes. The present project was directed toward the synthesis of such grids. We believe that we have made considerable progress and are within reach of having produced one such grid.

The most fundamental of the chickenwire covalent grids is graphene, in which there has been considerable recent interest.[1] The covalent grid system we investigated in this grant period is related to graphene and would likely have properties equally as interesting. We shall refer to it as porphene. The basic unit of the grid is Zn(II) porphyrin triply linked in the *meso-meso*, and both β-β positions on each of its four sides by carbon-carbon bonds to each of its four nearest neighbors in a square grid. The resulting fully conjugated grid would most likely be conducting, would possess a band stucture and have well defined pores (Figure 1). It appears likely that larger pores could be
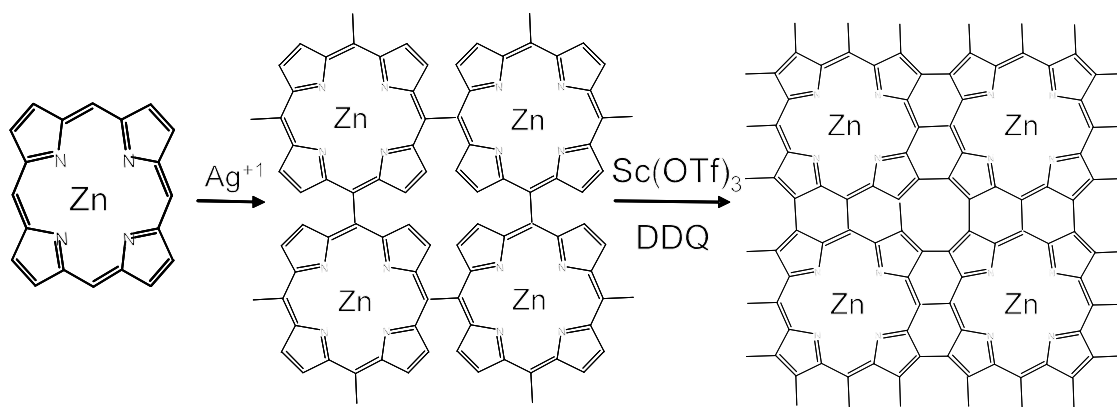

Figure 1. Synthesis of porphene sheets: (1) Zn(II)porphyrin is oxidatively *meso-meso* coupled with Ag^{+}, (2) *meso-meso* linked Zn(II)porphyrin is catalytically β-β coupled with DDQ under catalysis with scandium(III) triflate.

engineered if desired. The band structures of ethynyl-bridged 2-D porphyrin sheets have already been investigated computationally as possible optoelectronic materials of great promise.[2] The present work is an extension of our earlier investigation of regular grids of lanthanum porphyrin sandwich compounds[3] but will lead to grids linked in a manner that allows just a single planar conformation. This investigation is part of a broader interest in the development of a general procedure for the formation of covalent grids under conditions that permit a free choice of (i) lattice type and opening size and (ii) the chemical functionalization of the grid.

Our synthesis of 2-D porphene grids follows the chemistry developed recently by Osuka.[4,5] but is adapted to work at an air-liquid or liquid-liquid interface so that the polymerization of the porphyrin occurs under conditions that avoid insolubility problems resulting from the desired extremely high degree of polymerization and maintain the 2-D polymer in a perfectly planar conformation. If the dimensions of the synthesized porphene grid can be made to approximate an infinite plane, then the porphene band gap and other properties will be obvious analogs of graphene.

The interfacial synthesizes of a quasi-infinite sheet of porphite requires that the following task groups must be accomplished: (i) Application and dispersion of Zn(II)porphyrin onto a suitably chosen 2-D interface that can both support and hold the growing polymer in a planar conformation
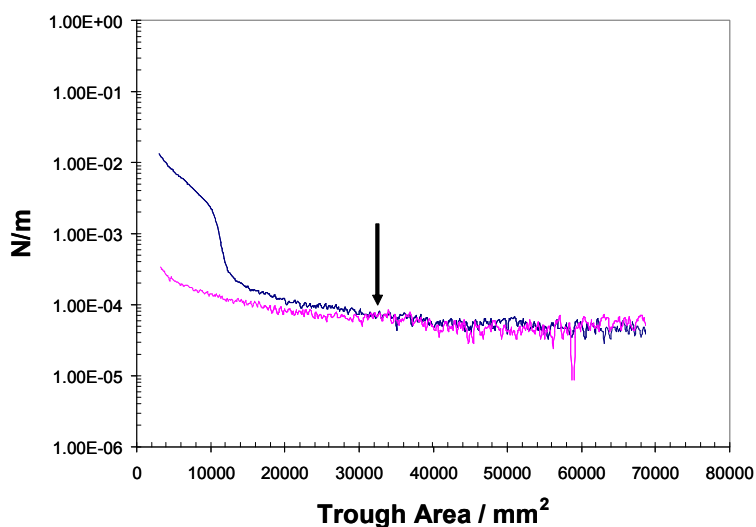
Figure 2. Isotherm for Zn(II)porphyrin. The arrow indicates where the isotherm (black) deviates from the baseline (magenta).

and permit the introduction of reagents for the coupling of the monomer units from at least one phase. (ii) Develop new or use known Langmuir-Blodgett (LB) methods to compress the monomer units to the ideal molecular spacing for facile and perfect coupling. (iii) Link the Zn(II)porphyrin through the oxidative formation of carbon-carbon bonds at the *meso-meso* positions. Develop assay methods to detect the extent of coupling in the polymerized monolayer at the liquid interface Use
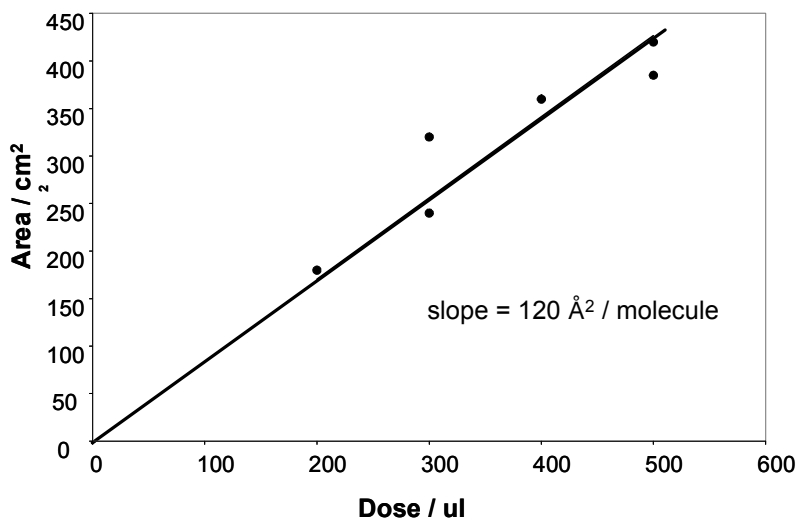

Figure 3. Plot of extrapolated face-down trough area vs. dose of 0.44mg/ml Zn(II)porphyrin in CH_2Cl_2. The mean molecular area for the face-down orientation of close-packed Zn(II)porphyrin is obtained from the slope.

the developed assay methods to optimize the coupling protocols based on Osuka's chemistry. (iv) Develop a method for the transfer and detection of a *meso-meso* coupled grid to a solid substrate. (v) Couple the meso-meso linked polymer in both β-β positions with Sc(III) triflate catalyzed
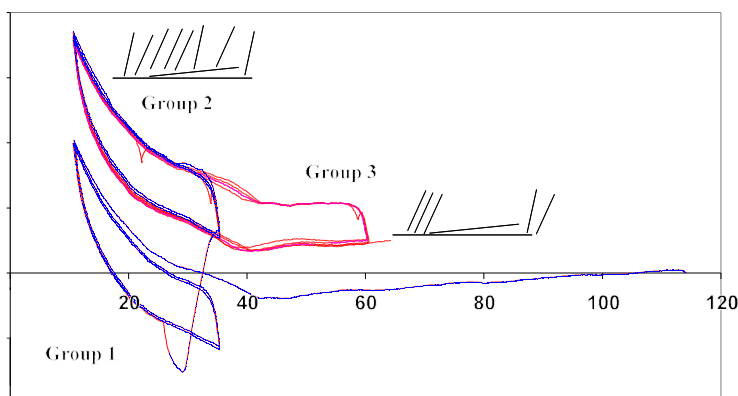
Figure 4. Repeated isotherms for Zn(II)porphyrin on the surface of water. Group 1 shows the set of initial isotherms. Group 2 shows the set of isotherms after the subphase is altered to 0.1 mM $AgNO_3$. Group 3 (*red*) shows the isotherms after the addition of $AgNO_3$ but after the barrier is allowed to expand.

oxidative coupling by DDQ to create a planar 2-D porphene grid. Develop assay methods to detect the degree of coupling, size of defects and planarity. Use the assay methods to optimize the β-β coupling protocols. (vi) Test the material properties of the porphene sheets including temperature dependent electrical conductivity, temperature dependent absorption, porosity and permeability, plasmon resonances, band gap and quantum confinement effects, thermal conductivity, etc.

Summary of Results

We have accomplished task groups (i - iii) in the single year that this grant was supported by the ARO.

Task Group (i): Initially we searched for two liquid phases that would permit the completion of both coupling reactions at one interface and avoid the complications of a transfer from one interface to another. After an extensive search it became apparent that a silicone oil-fluorocarbon or hydrocarbon liquid-liquid interface would be the ideal choice if the Ag^+ was dissolved into the silicone oil as the salt of a carborane anion, $CB_{11}Me_{12}(-)$. We knew that the lithium salt dissolved[6] and were hoping that the silver salt might, as well. For this purpose the silver salt was prepared, but it was found subsequently that the silicone oil, although very viscous, does not have sufficient surface tension for supporting the monomer. The high viscosity of the silicone oil made measurement and interpretation of the isotherms difficult because the Zn(II)porphyrin would slowly sink over a period of hours to the bottom of the trough. The long time constant of this process caused considerable confusion before it became evident that silicone oil was unsuitable as a subphase.   This left two problematic alternative approaches: The first is to use liquid Hg as the subphase as it is an ideal LB interface[7] and select an appropriate superphase after the Zn(II)porphyrin is applied the surface. Ag^+ would be added through an aqueous superphase followed by the scandium triflate and DDQ in an organic superphase. We were uncertain about interferences from bulk Hg and Hg cations, since the oxidation-reduction potentials of silver and mercury are similar, and and we are not certain that the Ag+ oxidation would succeed in close proximity to the Hg surface.   Although the advantages of a perfectly flat subphase whose chemical potential is

controllable are attractive, it seemed safer to start with preliminary experiments at the water-air interface and to introduce a transfer step between the coupling steps rather than as the final step. We could always return to the Hg subphase system at a later time. Also in this period we had to recover from a previous mishap that required a rebuilding of the LB-trough barrier and an alteration of the barrier sealing method to one that uses a dynamic O-ring seal; this was a painfully slow process.

The synthesis of porphene requires high purity starting material. We have adapted a literature[8] synthesis with more rigorous purification methods. We have also found that commercial sources offer very impure starting porphyrin.

Task Group (ii): Isotherms of Zn(II)pophyrin were measured to determine its mean molecular area in the face-down orientation within a close-packed array (Figure 2). The arrow indicates where the isotherm begins to deviate from the baseline, which is interpreted as the area at `which the applied dose of Zn(II)porphyrin molecules begin to interact with each other in an orientation which the porphyrin face is parallel to the interface. A later occurring steeply rising portion of the isotherm at a smaller area extrapolates to the mean molecular area that the porphyrin has when it compressed more fully to an edgewise orientation at the interface. Figure 3 shows the face-down trough area plotted as a function of the applied dose. The mean molecular area determined from the slope of this plot is 120 Å^2/molecule for the face-down orientation.

Task Group (iii): The goal of this group of tasks was to *meso-meso* link Zn(II)porphyrin by Ag^+ induced oxidation at the water-air interface and detect that this has happened. Figure 4 shows a series of repeated isotherms for Zn(II)porphyrin done at the air water interface. Group 1 shows repeated scans on the surface of water between 9 and 36 Å^2/molecule. These isotherms show no variation, as expected for an insoluble interfacial molecule and are constrained to traverse a region of the isotherm where they are packed edgewise. Group 2 shows a similar set of repeated scans collected after changing the subphase to 0.1 mM $AgNO_3$. Except for the offset in the surface pressure due to the change in the ionic strength of the subphase, there is no difference between Group 1 and Group 2. Under the same conditions, if the barrier is allowed to expand to a mean molecular area of 60 Å^2/molecule, the isotherm onset shifts to a larger mean molecular area on each successive scan and indicates that the mean molecular area is increasing This observation was anticipated if in the expanded space some of the Zn(II)porphyrin molecules will slip into the right conformation for *meso-meso* oxidative coupling. After this coupling has occurred it would make any subsequent flipping to an edge more difficult when the monolayer is recompressed and a distribution of coupled and uncoupled pophyrins would be expected to show, on average, an increased mean molecular area. This pattern repeats for each expansion until the mean molecular area distribution exceeds 65 Å^2/molecule (Figure 5).

This evidence for at least the partial oxidative coupling of Zn(II)porphyrin led to the further development of a more quantitative method for measuring the extent of the interfacial oxidative coupling by Ag^+. Zn(II)porphyrin was spread on the interface and compressed to 120 Å^2/molecule as determined from the experiments in section (ii). AgNO$_3$ was added to the subphase until its concentration was 0.1mM and after a variable interval, the unreacted Zn(II)porphyrin was washed from the surface with benzene and reduced to a known volume. The absorbance of the solution is assumed to be proportional to the fraction of unreacted monomer. The result for 0.1 mM AgNO$_3$ subphase concentration is shown in Figure 6. Several features of Figure 6 indicated that the system was not behaving as expected. First, only 60 per cent of the applied Zn(II)porphine could be collected from the surface even if no AgNO$_3$ was added. Second, the reaction only went to about 85 per cent completion. From difficulties we encountered in the purification of the Zn(II)porphyrin that we have synthesized it became apparent that Zn(II)porphyrin dissociates partially to Zn^{+2} and the parent porphyrin when in contact with the water interface. This dissociation was observed, by us, to differing degrees in any acidic solution that would dissolve Zn^{+2}. This observation nicely
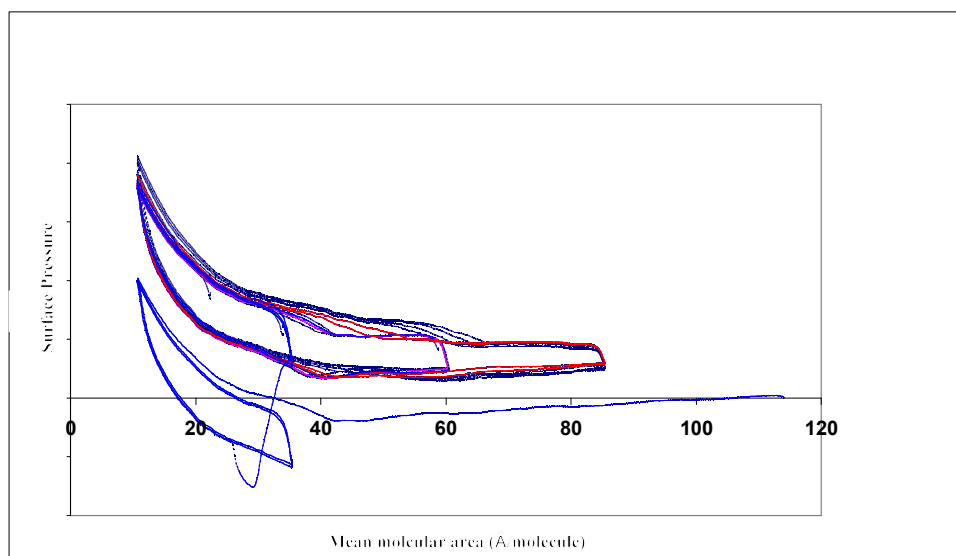

Figure 5. Full sequence of isotherms continued from Figure 4.

explains the observations of the kinetics wash-off experiment. Figure 7 shows the results for a similar experiment (AgNO$_3$ 0.2 mM) done on an aqueous subphase saturated with zinc acetate. Under these conditions nearly all the Zn(II)porphyrin applied to the interface can be recovered and the reaction goes to completion within the sensitivity of our spectrometer (<0.002 a.u.). Completion
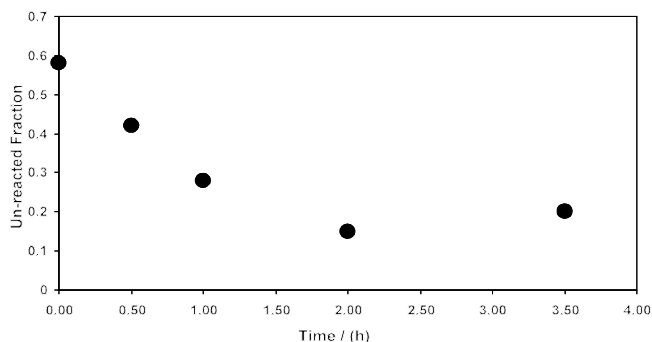

Figure 6. Plot of un-reacted fraction vs. time for Zn(II)porphyrin on 0.1 mM AgNO$_3$.

is defined here as the incorporation of monomer into a meso-coupled polymer of Zn(II)prophyrin of unknown MW that is insoluble in benzene. The half life for the coupling of Zn(II)porphyrin by this definition is 13 min.

Preliminary attempts to obtain mass spectra of the coupled polymer were made using the MALDI method to determine the molecular weight. Following the above protocols, the grid polymer was formed at the air-water interface above a shallow water pool standing on a MALDI
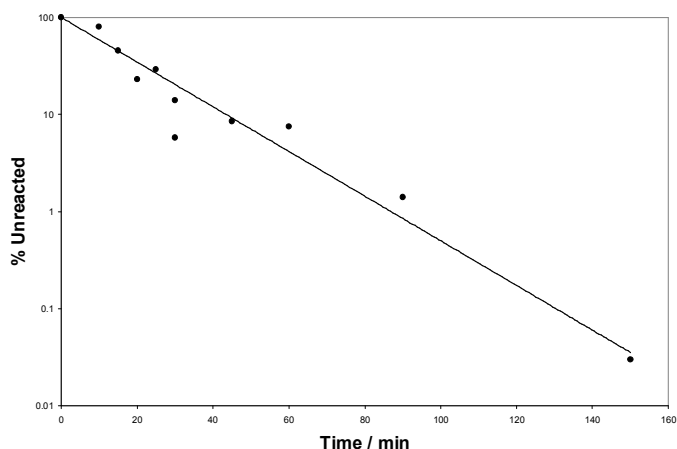

Figure 7. Log plot of unreacted Zn(II)porphyrin vs. time at the water-air interface saturated with zinc acetate. The half life is 13 min.

plate. After a time interval sufficient to permit the complete meso-meso coupling of the porphyrin the subphase was allowed to slowly evaporate leaving a residue of the AgNO$_3$ and the polymer. This portion of the MALDI plate was observed to be non-polar and no longer was wetted by CH$_3$CN.

Application of a sinapinic acid matrix resulted mass spectra with masses up to 10000 daltons when ablated by a N_2 laser. The pattern of peaks in the mass spectrum at this time is un-interpreted and depends strongly on the laser power and matrix. We are currently searching for optimal conditions that will generate an interpretable spectrum. Such spectra have been observed for linear polymers of ruthenium complexes.[9] We are hopeful that when MALDI mass spectrum is obtained these experiments will be publishable.

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